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PROCEEDINGS

of the

CITRUS PROCESSING CONFERENCE

Held at
Winter Haven, Florida
October 7, 1964

Agricultural Research Service
UNITED STATES DEPARTMENT OF AGRICULTURE

PREFACE

The Citrus Processing Conference is sponsored annually by the Southern Utilization Research and Development Division to present the results of recent studies in citrus chemistry and processing, and to provide for an exchange of information that will benefit future research.

This Conference was held October 7, 1964, at the Landmark Motor Lodge in Winter Haven, Fla., with M. K. Veldhuis, Chief of the Fruit and Vegetable Products Laboratory at Winter Haven, serving as General Chairman. The program was developed by B. H. Wojcik, Assistant Director, under the guidance of C. H. Fisher, Director, in cooperation with staff members, and advisers representing the citrus industry.

This report summarizes the statements of the various speakers during the conference, and gives an account of the discussions which followed. If further details are desired regarding any subject presented here, they may be obtained by communicating with the author concerned.

Numbers in parentheses refer to references or literature cited at the end of the article. The figures and tables are reproduced essentially as they were supplied by the writer of each paper.

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PROCEEDINGS OF THE CITRUS PROCESSING CONFERENCE

HELD AT WINTER HAVEN, FLA., OCTOBER 7, 1964

M. K. Veldhuis[1/], General Chairman

Session I

Howard W. Trumm[2/], Chairman

INVESTIGATION INTO THE HIGHLY VOLATILE FRACTION OF CITRUS JUICES BY GAS CHROMATOGRAPHY AND MASS SPECTROMETRY

by
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(Presented by G. L. K. Hunter)

The "Time-of-Flight" mass spectrometer is used for the direct analysis of flavor volatiles from aqueous systems. Γhe constituents are separated and purified in a specially designed gas chromatograph. The salient feature of the gas chromatograph is the thermistor type detector, which has high sensitivity and very low dead volume. The thermistor detector will detect all of the compounds the mass spectrometer detects such as nitrogen, oxygen, carbon disulfide, and water to which the flame gas chromatographic detector is insensitive. All of the material passes through the cell and through the oriface of a micrometering valve. The value meters the desired quantity into a short inlet tube leading to the mass spectrometer source. All of the sample can be directed into the mass spectrograph using the thermistor detector whereas part of the material is burned when using the flame detector. The sensitivity of the thermistor detector is of the same order of magnitude as the mass spectrometer.

Samples of volatile materials from citrus juices are obtained using an all glass and metal system. Helium is bubbled through the juice at room temperature, the vapors are passed over calcium chloride granules to remove a large portion of the water, and then led into a 3/8" x 15" stainless steel "U" tube. The tube is packed with glass helices and cooled in liquid nitrogen. After 4 to 5 liters of gas have been passed through the "U" tube, valves at each end are closed and it is fitted to the inlet system of the gas chromatograph. To inject the samples, the flow of carrier gas is directed through the "U" tube while warmed with a hot-air gun.

Before the sample is introduced onto the gas chromatographic column, the oven is cooled with liquid nitrogen to about -20°C. The sample is injected, and the column is allowed to to warm to 10°C., at which time the oven temperature is programmed at 3°/min. until 140°C. is reached. The detector and splitter valve oven is maintained at 150°C. The metering valve is adjusted to give a pressure of about 3 x 10^{-6}mm. in the mass spectrometer. Spectra are taken as the constituents are eluted from the column using a high speed oscillographic recorder.

1/ Chief, Fruit and Vegetable Products Laboratory, SURDD, Winter Haven, Fla.

2/ Libby, McNeill & Libby, Ocala, Fla.

A preliminary study was made on two juices to illustrate the technique. A 400 ml. sample of freshly expressed orange juice was obtained by gentle hand reaming. The procedure described above was carried out and carbon dioxide, acetaldehyde, methanol, ethanol, ethyl acetate, water, ethyl butyrate, α-pinene, sabinene, myrcene, ethyl hexanoate, and limonene were identified. These constituents have been previously reported by others; however, it is important to note that the analysis was completed in 4 hours by one person using only 400 ml. of juice.

Oranges that had been stored at 40°F. for 110 days were also analyzed as described above. The ethanol and terpene concentrations were about the same as found in the freshly picked orange; however, acetaldehyde and the esters were all but gone and the methanol/ethanol ratio increased. These data are preliminary and not necessarily meaningful. A more comprehensive study will be undertaken.

NEW AND RAPID ANALYSIS OF ALCOHOLS IN ORANGE OIL

by
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(Presented by M. G. Moshonas)

The difficulties encountered using the methods described in the literature for the analysis of alcohols in essential oils, such as removal of functional groups by derivative formation, distillation, or analysis of the whole oil, were overcome by using a liquid/liquid extraction procedure. The alcohol fraction was further purified by column chromatography, separated by gas chromatography, and analyzed spectroscopically. Nineteen alcohols have been identified.

The liquid/liquid extraction involves the partitioning of the whole oil between carbon tetrachloride and propylene glycol. The large nonalcoholic bulk of the oil dissolves in the carbon tetrachloride layer. The propylene glycol layer contains the alcohols and residual quantities of the other constituents. The alcohols are removed from the propylene glycol by the addition of a saturated solution of sodium chloride followed by extraction with ethyl ether. The ether is washed with water and dried with sodium sulfate. A portion of the residue, following removal of the ether, is placed on a basic alumina column and eluted with a solution of equal quantities of ether and hexane to remove residual carbonyls and hydrocarbons. The alcohols are eluted off the column with ethanol.

The residue, upon removal of the ethanol, was separated by gas chromatography. The material represented by each peak was collected and analyzed by infrared and mass spectroscopy. Further conformation was obtained, in some cases, by reduction to their parent structure which served to indicate the location of the hydroxyl function and the degree of unsaturation.

The alcohols n-octanol, n-decanol, linalool, citronellol, and α-terpineol, which have previously been identified as constituents of orange essential oil or essence by others, have been confirmed in the present study. The confirmation was obtained using infrared and mass spectroscopy by comparison with available spectra since these compounds are well characterized in the literature.

The alcohols n-nonanol, t-carveol, geraniol, and nerol, which have been tentatively reported to be in orange essential oil or essence by others, have now been identified to be constituents of Valencia orange cold-pressed essential oil.

The remaining ten alcohols that have not previously been found in orange oil are described here for the first time. Four of these alcohols have not been reported to occur in natural products.

Three of the six alcohols that do occur in natural products and that have not been reported in orange oil, heptanol, undecanol, and dodecanol were readily and confidently identified by infrared and mass spectroscopic analyses. The spectra of these materials have been well characterized and documented.

The fourth alcohol, elemol, was identified by comparison of its infrared spectra with that published by Pliva and Sorm[1/]. Mass spectral analyses of this material agreed with the elemol structure.

The remaining two alcohols, cis and trans-2, 8-p-menthadiene-1-ol were identified by comparison with spectra provided by Naves and Grampoloff[2/]

The four alcohols new to natural products have been identified as cis-carveol, 1-p-menthene-9-ol, 1-8-p-menthadiene-9-ol, and 8-p-menthene-1, 2-diol. Cis-carveol was shown to be identical to the product obtained from the reduction of carvone with lithium aluminum hydride. Reduction of 1, 8-p-menthadiene-9-ol with Platinum Black and hydrogen gave 1-p-menthene-9-ol. This latter alcohol, prepared by the hydroboration of limonene, was shown to be identical to the unknown. The last alcohol 8-p-menthene-1, 2-diol was shown to be identical to the material obtained by hydration of limonene oxide, the latter according to the method of Newhall[3/].

1/ Pliva, J., Horak, M., Herout, V., Sorm, F., "Die Terpene," V. O. I. Sesquiterpenes, Akademie, Verlog, Berlin. 1960.
2/ Naves, Y.R. and Grampoloff, A.V., Bull. Soc. Chim. p. 37, France. 1960.
3/ Newhall, W.F., J. Org. Chem.: 23, 1274. 1958

RECENT PROGRESS ON THE COMPOSITION OF LEMONS AND DESERT GRAPEFRUIT

by
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Because information on the chemical composition of grapefruit is far from complete, studies of the identities and amounts of the natural chemical constituents present in this fruit have been expanded. Emphasis is being placed on those classes of organic constituents that would be expected to contribute to the color, taste, and aroma of grapefruit or to exert pharmacological or physiological activities. Classes of compounds under investigation, which fall into one or more of these categories, are the carotenoids, polyphenols, steroids, and sesquiterpenes. Compositional studies on lemons, which have been underway for several years, also include these same classes of compounds. Detailed knowledge of the composition of these citrus fruits should be helpful in developing new and improved processed products.

As a result of this program, a detailed picture of the carotenoid pigments of lemon peel, endocarp, frozen concentrate, and crater-dried powder has been compiled[1/] Comparison of the identities and relative amounts of the individual pigments provide explanations for the color of the various portions of the fruit and juice products and show the

1/ Yokoyama, H. and Vandercook, C.E. (Unpublished data.)

effects of processing on the pigments. A similar study of the carotenoid pigments of desert grapefruit is now in progress. In addition, quantitative data on the total carotenoid and total sterol contents of commercial lemon and grapefruit concentrates have been obtained[2].

The sesquiterpene ketone, nootkatone, has been identified for the first time in grapefruit[3]. It is present in cold-pressed peel oils and in peel-oil-free juice of desert grapefruit. This ketone has been found to be an important factor in grapefruit flavor since it makes a significant contribution to the characteristic aroma associated with this citrus fruit. Studies are under way on the structure of nootkatone and on its flavoring properties.

Knowledge of the polyphenols of grapefruit is largely limited to the peel and peel oil fractions of the fruit. Very little is known about the edible portion (endocarp). Chromatographic examination of this portion of desert grapefruit has now shown the presence of numerous polyphenolic constituents including coumarin derivatives, psoralens, polyphenolic acid esters, and possibly glycosides and flavone and flavanone glycosides[4]. The main polyphenolic moieties released by enzymic hydrolysis have been identified and work is in progress on the glycosides and esters.

DISCUSSION

Question: How complete is the elution from the columns?

V. P. Maier: We are getting close to 100 percent elution off the columns.

Question: What is the degree of hydrolysis?

V. P. Maier: Of any particular constituent, it is very hard to get 100 percent hydrolysis. I think it must run up to 90 percent or something like that. This depends on how long you are willing to wait and how much enzyme you want to use and things like that.

Question: What did you use to elute the material from the column?

V. P. Maier: Benzene and acetic acid. A gradient was established by increasing the acetic acid concentration.

Question: What was the name of the sesquiterpene ketone you mentioned?

V. P. Maier: Nootkatone. It was first found by Erdtman in Alaska yellow cedar. I forget the scientific name, but that is where the name comes from.

Question: Is it commercially available?

V. P. Maier: No, Dr. MacLeod is in the process of getting a large batch of grapefruit oil and he is going to isolate some, but it is not commercially available.

Question: How is Dr. Horowitz coming with the sweet derivatives?

V. P. Maier: Very good. He has two of them--the one from neohesperidin is the most active and the one from naringin is close. They have been synthesized; they have been tasted; and a lot of people are looking at them to see whether they are interested in them commercially. I really can't tell you what is going on there--people don't like to talk about those things. But, he is also trying to fill in some of the gaps in terms of whether different substitution patterns on the benzene rings give better or worse sweetening properties. This is under active investigation right now.

Question: Was your work done on California lemons?

V. P. Maier: On California and Arizona lemons.

Question: Have you tried Italian lemons?

V. P. Maier: No, that is a good question. The work was done basically on California and

2/ Vandercook, C. E. and Yokoyama, H., J. Food Science (In press.) Yokoyama, H. and White, M. J. (Unpublished data.)

3/ MacLeod, W. and Buigues, N., J. Food Science, 29. 565. 1964.

4/ Maier, V. P. and Metzler, D. M. (Unpublished data.)

Arizona fruit because it was available. It is very difficult to get authentic Italian concentrate and be able to say for sure that it is authentic. We are now getting fresh fruit from Italy via Germany through New York and it is slow going. The fruit looks rather similar from the few samples we have had. This brings up another point--Florida lemons. We want to look at them so if anybody here makes lemon concentrate, we would be glad to have samples (a 6-ounce can) to look at.

Question: In separating carotenoids, do you start out with a counter current distribution system?

V.P. Maier: Dr. Yokoyama used column chromatographic techniques to separate and isolate the individual carotenoid pigments. The initial separation into the three general classes was made on a silica gel partition column. Each of these mixtures was then separated into individual pigments on a magnesium oxide column.

REVIEW OF THE FACTORS INFLUENCING BITTERNESS OF GRAPEFRUIT JUICE AND PRODUCTS

by
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(Presented by F. P. Griffiths)

It is perhaps fortunate that different individuals perceive tastes differently. It would be a gourmetless world if we all liked the same foods, or responded to sensations in the same manner. We might say it would be like a gray day--without highlights and shadows. Fortunately, there are many variations in taste, yet there is an overall pattern of response which decides that certain things are sweet, certain foods are sour, some salty, some bitter, and some tasteless. There are also such things as national preferences or norms which differ from country to country. The Mexican palate likes spicy foods, the Germans like acid or pickled foods, the French note flavor nuances which are of little concern to the English. The English like bitter marmalade and the Americans like theirs sweet.

Perhaps of particular importance to us is a belief, difficult to back up with facts or figures, that we are being conditioned to prefer blander, sweeter beverages. The New England hard cider, usually about half vinegar, is a thing of the past. The canned or bottled apple juice sold today has little resemblance to the full-flavored turbid juice we used to make 30 years ago. Soft drinks, all sweetened with sugar or artificially, have upped their sales 64 percent in the last 5 years to a record $2. 3 billion, or an estimated 227 bottles per person per year.

Orange juice remains a favorite beverage because it is, one might say, a beverage of moderation. It is not very acid; it is sweet enough to appeal to children, yet not too sweet for adults; it is not bitter; it has a pleasant aroma, a nice color, and a flavor that appeals to almost everyone. It is so good that we now have many imitations, from the powders Tang and Awake, to the insipid liquid that some dairies vend as Orange Drink.

Many people like the more pronounced flavors of good grapefruit juice, which is more acid, usually contains slightly less sugar, and has a tang or bitterness that is distinctive. Our experiences indicate that bitterness is acceptable within a rather narrow range, and that

young people, especially children, prefer much sweeter, less bitter, juice than adults. I am reminded of a Dennis the Menace cartoon of some time ago which showed him at the breakfast table, holding a glass and asking his mother mother, "Mom, what's wrong with this orange juice?" And his mother's reply, "Son, that's not orange juice; that's grapefruit juice." We had a somewhat similar experience when we were trying different blends of juices on the schoolchildren next door to our laboratory and received thank-you notes from the third grade, one of which said, "I liked the drink you gave us because it did not hardly taste like grapefruit juice at all."

This paper seeks to review the factors that influence bitterness of grapefruit juice and products, and some of the work that is in progress to develop methods of more accurately measuring bitterness and to control the level of bitterness in grapefruit or products containing grapefruit. Much of the information is not new; in fact, I can be accused of "carrying coals to Newcastle."

The major cause of bitterness in grapefruit is naringin. Eleven years ago, Kesterson and Hendrickson of the Citrus Experiment Station at Lake Alfred, Fla., published an excellent bulletin, No. 511, about naringin. USDA Agriculture Handbook No. 98, "Chemistry and Technology of Citrus," (1962) presents a summary of information on bitterness. Horowitz of the USDA Pasadena Laboratory has recently published a chapter, "Relations Between the Taste and Structure of Some Phenolic Glycosides," in the book, "Biochemistry of Phenolic Compounds," edited by Harborne, Academic Press, August 1964. Some of the information I have is from these references.

Figure 1 shows the structural formula of naringin and the way it can be split to form prunin and the aglycone naringenin. Naringin at a concentration of 0.05 percent is intensely bitter and the bitterness lingers or is apparent for a long time. Prunin is about one-third as bitter as naringin, and the bitterness and after-taste are of short duration. Naringenin is tasteless. One of the difficulties we encounter when tasting for bitterness is loss of taste acuity--taste buds quickly become unresponsive to variations in bitterness.

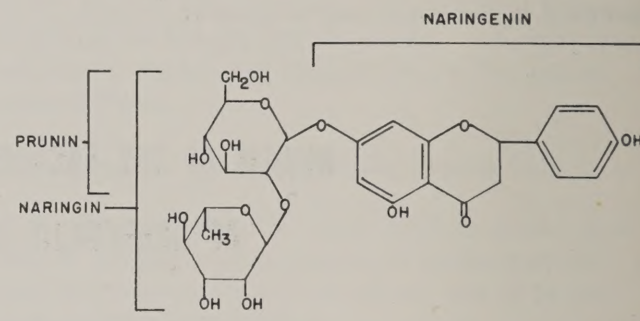

Figure 1.--Showing chemical configuration and interrelationship of naringin, prunin, and naringenin.

Although naringin is the major flavonoid of grapefruit, other flavonoids are known to be present. Poncirin, neohesperidin and rhoifolin occur in appreciable quantities. Horowitz lists poncirin as being as bitter as naringin, neohesperidin as being one-tenth as bitter, and rhoifolin as tasteless.

Bitterness is influenced by variety, type of rootstock, soil, water, and various climatic conditions. Although Texas Ruby Red grapefruit is reported to contain the most naringin, it is usually rated as less bitter than Florida or California fruit. Grapefruit raised in Central and South America is sometimes so bitter as to be unpalatable (a varietal difference). There is a wide variation in bitterness throughout the growing and maturing season. Studies with C^{14} confirm the assumption that naringin is formed early in the growth of the fruit and as the fruit enlarges, dilution occurs (Lime, unpublished). Very small green grapefruit contain as much as 40 percent of the dry weight as naringin when measured by the Davis method. Table 1 shows seasonal variation of naringin as percent of dry weight and as amount of naringin per fruit.

Table 1. --Seasonal variation of naringin in Texas Ruby Red grapefruit

Date	Size mm.	Percent naringin of dry weight	Naringin per fruit gr.
4-25	17	40	0.27
5-9	24	38	.78
5-23	37	23	1.5
6-20	55	20	1.7
8-1	67	20	1.8
9-12	82	14	1.9
10-10	80	15	1.6
11-15	92	13	1.5

After the fruit has reached maturity, bitterness in the juice continues to decline. During February, March, and April the decline in bitterness as measured by taste may show a marked decrease, whereas chemical tests for flavanones do not always show an equivalent reduction.

A mature grapefruit contains different concentrations of naringin in different parts of the fruit. Table 2 shows the variations we found in fruit.

Table 2. --Distribution of naringin in red grapefruit (January 23-30, 1956)

Juice extracted from juice sacs. (pct.)	Juice sacs blended (pct.)	Septum or rag (pct.)	Albedo (pct.)
.003	.046	0.55	2.48
to	to	to	to
.007	.092	.78	2.90 1/

1/ Naringin concentration is higher in small fruit than in large.

Taste is and always has been the basic method for measuring bitterness. Davis (Ind. Eng. Chem., Anal. Ed., 19: 476-8. 1947) published a method for determining flavanones in citrus fruit which has had wide application. Although the Davis test is useful, it is limited in its application and measures flavornoids which are not bitter. We became aware of this discrepancy in 1953 when comparisons of Texas pulp fortified juice with California juice showed that in spite of having a higher Davis value, the Texas juice was less bitter. This led to the supposition that other flavonoids were present which were Davis positive but were less bitter than naringin.

Horowitz and co-workers have shown that the bitterness of flavonoids depends in a large measure on the sugar linkage. If the aglycone naringenin is bonded through the 7-hydroxyl to the rhamnosyl-glucose disaccharide, and if the rhamnose-glucose linkage is through the C_2 hydroxyl of glucose as in neohesperidose, the compound is bitter. If the sugars are linked together through the 6-hydroxyl group of glucose to form a rutinoside, the resulting naringenin-7-β-rutinoside is not bitter. (Figure 2) Horowitz and Gentili isolated this compound from the peel of Navel and Valencia oranges and also isolated a compound which is not bitter but is isomeric with poncirin. This has tentatively been identified as isosakuranetin-7-β-rutinoside. The nature of the flavonoid aglycone also affects bitterness. Naringin and rhoifolin both contain the 7-β-rhamnosyl glucoside; but the former is bitter, the latter is not. Figure 3 shows molecular models of their respective aglycones naringenin and apigenin. It can be seen that the nonbitter rhoifolin has an aglycone, apigenin, which is essentially planer, while naringenin, the aglycone of naringin is nonplaner. Since the C_2 carbon of naringenin is asymetric, it is interesting to speculate that the two possible stereo isomers may have a different taste response. We are conducting investigations along this line. Rowell and Beisel (J. Food Sci. 28(2): 195-197. 1963) speculate that grapefruit may become less bitter because of the conversion in the mature fruit of naringin to rhoifolin.

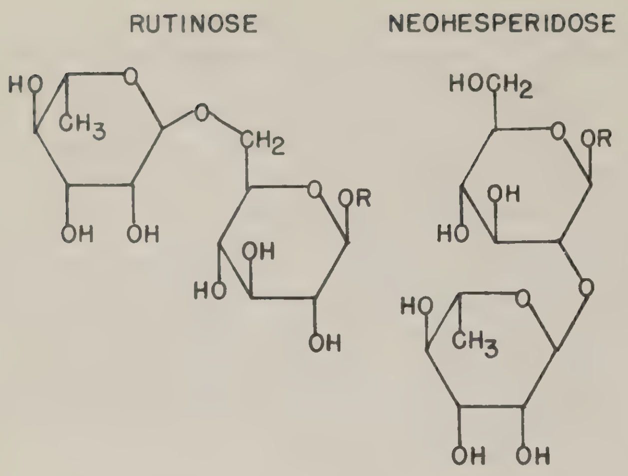

Figure 2.--Showing (nonbitter) 6 linkage for rutinose and (bitter) 2 linkage between rhamnose and glucose in neohesperidose sugars. R = aglycone, attached to glucose.

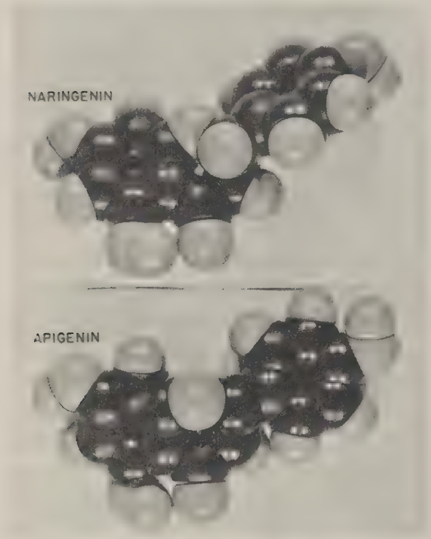

Figure 3.--Molecular model showing nonplaner configuration of naringenin and planer configuration of apigenin.

It is obvious that if a system exists in the grapefruit that can change the sugar linkage in naringin to that of the nonbitter rutinoside, changes in bitterness will occur irrelevant to total flavoronoids present as measured by the Davis or similar tests.

Methods of separating and measuring bitter components are now the subject of intensive investigations. The Western Utilization Laboratory has a line project, No. W3 1-125, directed by Dr. Horowitz, on composition of desert grapefruit. The USDA has a research contract with Dr. Wender and associates of the University of Oklahoma. The objective of this contract is stated: "To define changes which occur as grapefruit matures, in total flavonoids, in poncirin; and in the amount, location and structure of the naringin and naringin-derived compounds; in order that scientific control methods and blending procedures may be developed for the processing of uniformly flavored grapefruit products through the processing season." Dr. Wender and his group are developing methods of chromatography that resolve the flavornoids from grapefruit into many more than have previously been noted. They are using a photofluorometric technique to quantitatively measure the amounts present. They have separated a second naringenin rhamno-glucoside, which appears to be nonbitter and which may be the nonbitter 7-β-rutinoside. On the basis of a very limited sample they report the ratio of bitter naringin to naringin 2 (nonbitter) in midseason juice was 3 to 1. In late season juice the ration was approximately 2 to 1. The total naringin values of late season juice was approximately 75 percent of that of midseason juice, the decrease which occurred being almost entirely in the amount of bitter naringin. This information helps to explain the discrepancies which occur when measuring bitterness by the Davis procedure. These suggested analytical procedures will open a new field of research on the standardization of grapefruit products.

Bitterness in grapefruit juice can be controlled to some extent by mechanical means. Because bitterness is lowest in juice within juice sacs and highest in rag and albedo, low extraction pressures and light finishing pressures tend to keep bitterness at a minimum. We believe that if a two-stage extraction procedure could be developed, the first light extraction would give a superior juice. The second extraction, yielding "everything but the squeal," might be debittered by chemical methods or used as a concentrate for flavoring bottled drinks.

In our study of pulp fortification of juice from Ruby Red grapefruit, we found that increasing pulp content increased bitterness.

Figure 4 shows that in early December (December 4) an increase in pulp content caused not only an increase in color, but a sharp increase in naringin values. Figure 5 shows that six weeks later (January 15) much more pulp was required to cause a corresponding increase in bitterness. With the new analytical techniques, we intend to study how this decrease in bitterness occurs.

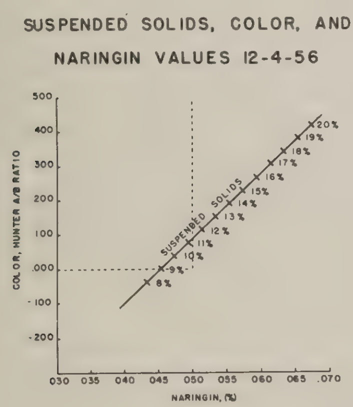

Figure 4.--Influence of suspended solids on bitterness and color of early season red grapefruit.

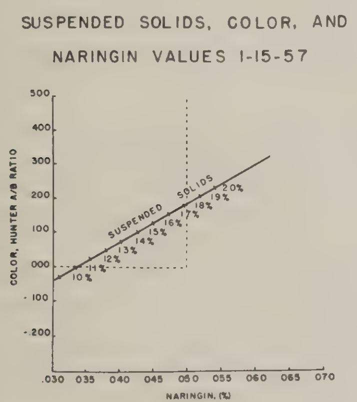

Figure 5.--Influence of suspended solids on bitterness and color of midseason red grapefruit.

Following the discovery by Dr. Ting (J. Agr. Food Chem. 6: 546. 1958) that pectinase contained an enzyme that caused loss of bitterness of grapefruit juice and the development of a source of this enzyme, naringinase, by workers at Rohm and Haas, we studied its application to the debittering of juice and pulp of Texas grapefruit. (Griffiths and Lime, Food Technol. 13(8): 430. 1959). We were able to debitter pulp from Ruby Red grapefruit and use it to add color without adding bitterness to the juice. With the enzyme preparations available to us, it was necessary to pasteurize juice before adding naringinase to avoid loss of cloud. Either naringinase contains pectinesterase as an impurity or it has a synergistic effect on the pectinesterase present in unheated juice.

The USDA has recently negotiated a research contract with Dr. Wenzel and associates for more thorough investigation of the possibilities of enzymatic debittering of grapefruit and and grapefruit products. The objective of this research is to conduct investigations to develop a practical and efficient pilot plant process for the manufacture of enzymatically debittered grapefruit juice and products with improved flavor, product stability, and storage characteristics.

As I reported last year, the Weslaco Laboratory found that certain resins would selectively debitter grapefruit juice without markedly affecting flavor. Nylon and polyvinyl pyrrolidone resins have been used for this purpose. In addition to loss of bitterness, resin treatment results in improvement in the flavor of immature or off-flavored juice. Resin treatment does not affect vitamin C content of the juice. We expect to continue our investigation of the possibilities of resin treatment. Polyamide (Nylon) and polyvinyl pyrrolidone (Polyclar AT) chromatography were investigated by the Weslaco Laboratory and are being adapted and improved by Dr. Wender's group for separating flavonoids. We hope that analytical procedures describing their use will be published soon.

It is obvious that bitterness of grapefruit juice can be reduced by dilution. Mr. R. W. Olsen of the Florida Citrus Experiment Station, in 1961, served grapefruit drinks made by fortifying a diluted grapefruit juice with sugar and acid. The Weslaco Laboratory has developed and published several formulations for so-called concentrate, which fortify grapefruit juice with sugar, acid, flavors or other fruit juices. A formulation we especially like is a grapefruit-orange-strawberry combination shown in Table 3. When diluted with three parts water, this makes a refreshing, 100 percent fruit drink. And as the youngster said,

"You can't hardly taste the grapefruit," even though it provides about 50 percent of the volume of fruit juice used.

Table 3. --Grapefruit-orange-strawberry punch concentrate (3+1)

Grapefruit juice	Acid, 1.36 pct. --Brix, 9.5	1800 ml.
Lemon concentrate	Acid, 32.6 pct.	180 ml.
Strawberry puree	(from 3+1 frozen berries) Brix, 33	450 ml.
Orange concentrate		150 ml.
Orange oil emulsion 1/		0.45 ml.
Sugar		1500 gr.

Brix of concentrate, 46.5°. When diluted, Brix, 13.0°, Acid, 0.65 pct.

1/ Dodge & Olcott Colloidex No. 1.

CONCLUSION

Much work is now in progress on methods of determining bitterness in grapefruit and on procedures for reducing bitterness. We believe that the next year will see the publication of quantitative methods of separation and analysis of the flavonoids of grapefruit. These procedures will be of great assistance in studying flavonoid formation in the fruit and in the studies on methods of controlling bitterness. Research now being initiated on the pilot plant aspects of enzymatic debittering of grapefruit juice should aid in evaluating the industrial possibilities of this process. Resin debittering also may have industrial possibilities.

The use of grapefruit juice in new blends and drinks offers possibilities for increased use of grapefruit juice. The next year or two should be exciting ones in developing information and processes of value to the grapefruit processing industry.

SEPARATION PROCEDURES AND IDENTIFICATION OF HYDROCARBONS IN CITRUS OILS

by
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(Presented by G. L. K. Hunter)

An analytical system has been developed for the identification and approximation of sesquiterpenes as well as terpene hydrocarbons in citrus oils.

A method of distillation using an Arthur F. Smith "Rota-Film Molecular Still" has been adapted in which the oil is flash vaporized requiring short exposures at elevated temperatures. The distillation process makes large quantities of material available for analysis. The terpenes are removed from the whole oil at 80°/1.0 mm. The residue is redistilled in the molecular still at 100 to 110°C. at 0.25 mm. to give a fraction containing the sesquiterpenes.

The oxygen containing materials in each distillation fraction were removed by percolation through basic alumina with hexane as the

eluant. A negligible change was noted in the terpene yield; however, the yield of sesquiterpenes was reduced by a factor of ten.

The terpene fraction has previously been well characterized. The sesquiterpene fraction, after removal of the hexane, was separated by gas chromatography.

The eluted constituents were condensed into suitable vials and analyzed by infrared and mass spectroscopy and by chemical means. The compounds found in orange oil, in addition to ylangene and farnesene that have previously been reported by others, are α- and β-copanene, β-elemene, β-ylangene, caryophyllene, α-and β-humulene, valencene and Δ-cadinene. β-copaene, β-ylangene and valencene are sesquiterpenes that have not been characterized before.

The above procedure was used on other essential oils when large quantities of material for structure study and spectral reference data was needed. This procedure was not suitable for rapid evaluation of the hydrocarbons in essential oil nor for quantitative determinations.

Once the mass spectrum of a compound had been catalogued its presence could be detected in future analyses of any oil providing approximately 0.05 μ 1 of material could be isolated. This allowed the procedure to be miniaturized which was accomplished by placing as little as 1-2 ml. of the whole oil onto an alumina column and removing the hydrocarbons by elution with hexane. Upon removal of the hexane the residue was separated by gas chromatography. Low loaded columns, which result in improved resolution, were used since very little material was needed for positive identification.

The terpene analysis was accomplished by using 2.5 μ 1 of the mixture. In order to obtain an analysis of the sesquiterpenes, it was necessary to increase this quantity by two orders of magnitude. A semi-quantitative comparison between the two curves can be visualized by replacing the terpene chromatogram, obtained during the sesquiterpene analysis, by the one obtained using 1/100 (2.5 μ 1) of the sample.

The materials represented by each of the gas chromatographic peaks were condensed in 6" glass capillary tubes for further analyses. Each of the tubes, after sealing one end, was inserted into the mass spectrometer for confirmatory identification.

Various citrus oils were analyzed including orange, grapefruit, tangerine, lemon, and lime. Also, comparisions were made between juice oil and peel oil.

DISCUSSION

Question: Where does the carbon dioxide come from?

G. L. K. Hunter: Carbon dioxide is indigenous to the fresh fruit. We think the carbon dioxide is readily lost from freshly expressed juice and other highly volatile flavoring materials are lost along with it.

Question: Why did you use the thermistor detector instead of a flame detector?

G. L. K. Hunter: The thermistor gives the same magnitude of response as the mass spectrometer. The flame detects materials whose concentration is below the limit of the mass spectrometer. Also, the thermistor does not destroy material and responds to such materials as oxygen, nitrogen, carbon disulfide, and water which the flame does not.

Question: Would the thermistor detect hydrogen sulfide in the orange juice? Have you found any?

G. L. K. Hunter: Yes, it would. If hydrogen sulfide is in the juice it is being covered up by the carbon dioxide and we haven't detected it. There are methods by which H_2S can be monitored using the mass spectrometer and we will pursue this more diligently in the future. Some modifications are being made to the mass spectrometer such as predynode gating, which will remove the helium when it is set on mass 4, extended flight tube, and a continuous mode. These are designed to increase the sensitivity and resolution. The additions are made possible by the Florida Citrus Commission.

Question: You mentioned that the ethanol and the methanol area gave a typical orange aroma. To what do you attribute this?

G. L. K. Hunter: Ethyl butyrate at this time.

Question: Do you think that the orange flavor is due to a relationship between ethyl butyrate, ethanol, and methanol?

G. L. K. Hunter: The gas chromatogram shows only three peaks and, by mass spectrometry, identified as ethyl butyrate, ethanol and methanol. This doesn't mean that there is no additional material under the peaks. If the material represented by this area is removed, the orange odor will also be removed.

Question: I know the data are preliminary, but in view of what you have pointed out, do you plan to store fresh orange juice under carbon dioxide to see if it has any effect on flavor?

G. L. K. Hunter: We haven't made any plans for storage studies at this time. We plan to study the changes that take place in the volatile portion of fresh juice with time. This is a study on storage without additions. We still have to work out a procedure in which all of the volatile compounds can be evaluated. Additions of various naturally occurring materials to the juice will certainly follow.

Question: What concentration is needed in order to obtain a mass spectrum?

G. L. K. Hunter: A few micrograms. The ethyl hexanote peak in the chromatogram, which extended 1/4" up from the base line, was of sufficient concentration to give a good spectrum. It is nice to have enough material so that various portions of the curve can be monitored by mass spectroscopy. Peak purity can often be determined in this manner.

Question: Does carbon dioxide come from the juice?

G. L. K. Hunter: Yes, it comes from the juice.

Question: Stored oranges have less flavor. To what do you attribute this?

G. L. K. Hunter: The stored orange had a distinct inferior flavor. We don't really know what materials are lost at this time, however, the preliminary studies show differences and this is encouraging.

Session II

O. R. McDuff [1/], Chairman

MARKETING OF PROCESSED CITRUS PRODUCTS

by
J. H. Child
Minute Maid Co.
Orlando, Fla.

I was certainly pleased to be invited to appear on your program, and especially to talk about marketing. I feel that the citrus industry today is standing on the threshold of new marketing opportunities and horizons.

Many of us have strong opinions about how we should market our products, but I would hasten to add that these opinions are not really worth very much unless they reflect the attitudes, wants, and needs of the consumer. Today, the consumer wants variety in taste, products, packages, and price. We must, therefore, be consumer oriented--in our planning to insure that we are selling citrus solids in whatever form the consumer wants. This means that we are in the business of selling a variety of juice, drink, and ade products.

1/ Adams Packing Co., Auburndale, Fla.

Up to the end of World War II the U.S. economy was mainly production oriented. We've all heard the story about the automobile manufacturer who is supposed to have said "The buyer can have any color he wants so long as it's black!" Since World War II we have seen tremendous strides in marketing technology and we find today that well informed management has adopted what we might call the marketing approach or marketing concept in running their business. This simply means that in the highly competitive market place today the consumers' wants and needs must be a prime consideration in all planning.

Putting it another way we must be oriented toward the people who consume our products rather than the product itself. This will help us us do a better job of filling present market needs, but more importantly, in the long run this will give us an opportunity to find new markets--to reach the many millions of American families who are not as yet regular consumers of our healthful and refreshing Florida citrus products. There are many ways to look at the consumer today:

As an economic unit.

As a market.

As buying power.

As a source of income.

As the holder of the family purse strings.

But I like to think of the consumer as a daily hero who works daily miracles. We need to know as much about her as possible--her needs and wants and her reaction to our products. We need to know:

How well she likes our products.

How often she uses our products.

How much she is willing to pay for them.

The time of day she uses them.

Does she consider them convenient?

Does she use them at home, away from home, or both?

Does the product have a health connotation in her mind?

Does her husband like the product?

Do her children use it?

What motivates her, etc. ?

To successfully market our products we need to know all her attitudes, opinions, and habits--why these habits have been formed and how we can effectively take advantage of them.

In the last two decades, American business has gone to incredible lengths to satisfy the consumer. Consider the automobile business; there is a size, color, style and price to appeal to almost every individual in the country. We see the same trend in food and beverage products. We are all keenly aware of this and I think there is a good lesson to be gained. In almost all instances the market did not contract but expanded with the development of new products which appealed to more people. I have a good example of this in my own home--as I'm sure each of you do in your own home. For 11 years one of our daughters absolutely refused to eat cereal at breakfast--at least until 2 weeks ago. Now she eats with great gusto a new product that has marshmallow bits sprinkled through it. The cereal manufacturers have gained a new consumer simply because they made a special effort to appeal to a particular taste.

For many years soup was available only in a can, except for a limited selection of bouillon-type products. However, today we also find soup products in dehydrated form and in the freezer cabinet. Similar developments have occurred in almost every product category that comes to mind; to name just a few--soft drinks, coffee, breakfast cereals, dog food, cake mixes. And of real significance to us we find the same trend occurring in the consumption pattern of fruit juices and drinks!

Today, there is a significant volume of fruit drink products being purchased by the

consumer. I refer here to those products that are less than 100 percent pure juice but still contain a substantial amount of fruit solids. To illustrate this I'd like to cite a couple of interesting figures. Total retail consumer purchases of fruit juices and drinks currently run close to 800 million single strength gallons per year. These 800 million gallons are made up of the following product categories: Frozen orange juice, other frozen juices, chilled juices, single strength juices, canned fruit drinks, and frozen drinks. The last two items--canned fruit drinks and frozen fruit drinks--accounted for 40 percent of the total volume this summer (1964) during the months of June, July, and August.

The consumer apparently likes these products and is using them in significant quantities. An obvious conclusion might well be that the consuming public will use more and more of these canned and frozen drink products as we direct more and more advertising and merchandising toward these products. Our marketing research studies make one fact about the consumer crystal clear and that is--we can't reach and satisfy all consumers with any one single product. For example, despite the tremendous volumes that this industry has generated in frozen orange juice, there appear to be limitations with this product, which has long been the backbone of our total Florida citrus industry. Let me mention three important limitations:

1. For years prior to the December 1962 freeze, the percentage of U.S. families buying frozen orange juice in any 1 month held consistently at or below the 30-percent level.

2. To a large extent frozen orange juice is confined to home use.

3. Also, as most of us know, nearly all the families who use orange juice serve it only for breakfast.

This marketing information is a valuable tool for all of us in the industry and should point us in the right direction in our marketing efforts. Certainly if orange juice has so completely captivated the breakfast market, it is quite obvious that we must develop new citrus products for use by these folks at other times of the day, and other new products for those consumers who simply refuse to purchase full-strength orange juice.

Now let's consider the behavior pattern or buying pattern for individual families. Recently, we, in Minute Maid Company, did a special study to find out what families bought what juice and drink products. For example, we wondered if a certain group of families bought mainly frozen orange juice and, on the other hand, if another completely different group of families bought mainly canned fruit drinks. The results of this study showed us conclusively that the average household uses a variety of juice and drink products. For example, in examining the buying pattern of families who use frozen orange juice we find that these same families used a multitude of other juice and drink products. Likewise, we analyzed families who bought fruit drink products and found these same families also consume a great variety of juice products.

So here is further proof that the consumer likes and uses a variety of drinks in addition to pure juice products. Several consumer surveys that we have conducted show very clearly that drinks move us out of the old "breakfast only" category and into the refreshment field. This opens up entirely new horizons for us and should certainly be a key consideration in our current market planning. We in the citrus industry must listen to the consumer, keep our finger on her pulse, and give her what she wants--or someone else will!

Right now we have a new development in the market place that represents a real challenge to Florida's citrus industry. A frozen synthetic product is being promoted and advertised on a national basis and is aimed directly at the consumer of our products and particularly the consumer of frozen orange juice. This product already has carved out a significant slice of the market, and it will carve out even more of our market unless we move now to intelligently revise our basic marketing attitudes--unless we stop selling our products and begin to market them.

So in closing I'd like to say again--it's the consumer who calls the tune in a free enterprise system! And it's my responsibility, your responsibility, and the combined responsibility of all in our dynamic Florida citrus industry not only to develop the products necessary to fill our untapped markets but to aggressively market these new products to their fullest potential.

DISCUSSION

Question: Is information being collected on powders such as Kool-Aid and Tang?

J.H. Child: This sort of product represents good volume unit wise, but it is not so big dollar wise. Yes, data on Kool-Aid and Tang is being collected.

Question: Are these Market Research Corporation figures?

J.H. Child: The figures that I used are Market Research Corporation of America Consumer Panel figures. We have subscribed, as has the Industry, to this service for many years and it gives us a pretty good fix on the trends that are occurring in the market place.

Question: This is a dirty word, but what is the increase in sales on the artificial market?

J.H. Child: The one that I referred to--the rate of sales has climbed fast. This frozen synthetic product had about an 8 percent share of frozen orange juice purchases back in June (1964) and at the latest reading it was better than 12 percent.

Question: Is that a synthetic juice?

J.H. Child: Yes, completely.

Question: Are these figures based on total citrus sales?

J.H. Child: No, just frozen orange juice.

COMPOSITION OF ORANGE JUICE CLOUD

by
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(Presented by W. C. Scott)

Considerable attention has been given through the years to methods for stabilizing cloud in orange juice, but until recently there has been little information on its composition. Various methods for recovering cloud from orange juice were investigated. Most practical method found consisted of classifying suspended solids by sedimentation rate: Free and suspended solids were removed in the Supercentrifuge operated at low speed with high flow rate (sediment A), then the ordinarily nonsettleable solids were recovered by centrifuging at low flow rate and high relative centrifugal force (sediment B). Repetition of high speed centrifuging resulted in the recovery of small amounts of very fine solids (sediment C).

Centrifuge sediments were treated with 4 volumes of hot 95 percent ethanol. Solids insoluble in this medium were further extracted with 80 percent ethanol, acetone, and n-hexane. Alcoholic extracts were freed of alcohol in vacuo and the aqueous residue extracted with hexane. All acetone and hexane extracts were combined and evaporated to dryness to measure the lipid content of the sediments. Aliquots of the aqueous solutions were dried on sand in vacuo to measure the alcohol-soluble content of

the sediments. Solids insoluble in the solvents used (SI) were air dried and weighed, with final moisture content being determined in vacuo.

Samples of orange juice were obtained from commercial canning and concentrate plants for most of these studies. The work covers the latter part of the 1961-62 and the 1962-63 seasons, and includes 6 samples of juice from early fruit, 4 from midseason fruit, and 10 from Valencia fruit. Also, in 1964, midseason and Valencia fruit were dissected by hand, and solids from albedo, rag, pulp, and juice were analyzed in the same manner as were the centrifuge sediments.

Variations in alcohol-solubles reflect mainly the wetness, or residual juice content, of the centrifuge sediment. Of course, the A sediments were highest in this component, due to having been separated at low centrifugal force. Because of this, the lipids and the solvent-insolubles (SI) were proportionally lower when expressed as percent of total dry solids. The ratio of SI to lipids, however, is not influenced by the accompanying juice solids. The SI contents of A sediments were about nine times as great as the lipids, while in the finely divided solids (B and C sediments) the ratio was only about 3:1. This indicates that the lipid material in the juice was dispersed in such small particles that extremely high centrifugal force was required to precipitate them and also that lipids constituted approximately one-fourth of the weight of the finely divided material contributing to stable cloud.

Composition of Solvent-Insolubles: Ash content was fairly constant among varieties. Finely divided solids (B and C sediments) contained slightly less ash than the free and suspended solids (A sediment). Among the dissected parts of fruit, albedo, and rag showed ash content approximately the same as the centrifuge sediments, while SI from the strained juice showed very high ash. Pulp was intermediate.

Nitrogen (Kjeldahl) and phosphorus content of the SI from B and C sediments were considerably higher than from the sediment A and highest of all in the strained juice. SI from albedo and rag contained very little nitrogen.

Carbohydrate content of SI was classified into pectins, hemicellulose, and cellulose. Material soluble in 0.05 N NaOH and precipitable with ethanol were considered as pectins; those soluble in 4 N NaOH but insoluble in ethanol as hemi-cellulose; and solids remaining, as cellulose. As would be expected, the B and C sediments were richer in pectin and much lower in hemicellulose and cellulose than the A sediments.

No appreciable differences were found due to variety or season. When oranges were dissected by hand, and the sections pressed in cheesecloth, the juice obtained had optical density above 1.5, which is as dense as any of the commercial juices examined. This indicates that mechanical disintegration of structural tissue is not required for adequate cloud, although it may contribute additional suspended matter.

A SURVEY OF FOAM-MAT DRYING

by
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Engineering and Development Laboratory
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The purpose of the foam-mat drying project is to offer a means of well and cheaply drying liquid foods. Drying itself serves to preserve food, to reduce storage, shipping and packaging charges, and to present a new and versatile product form. Foam-mat drying--warm air dehydration of stable foams--also provides powders of good quality and ready reconstitution.

In the summer of 1959, John Randall, then a junior at the University of California, temporarily employed at the Western Utilization Research and Development Division, and I started working with fluid flow. As chemical engineers we were rather academically interested in the peculiar rheology of foams which are both compressible and pseudoplastic. The latter property means that flow increases more rapidly than pressure drop. We found ways to make stable, if not necessarily edible, foams from various foods. We immediately found that these foams air dried very rapidly, retaining much of the foam structure in the dry form.

Bob Graham and I then devised a straightforward process for continuously drying such foams. We obtained and learned to disperse edible foam stabilizers--first sucrose esters, then monoglycerides, and finally soluble proteins with gums. This last was at the suggestion of Ken Gunther, of Gunther Products. We learned to use continuous mixers to subdivide the bubbles added to the liquid stream from gas bottles. We originally wiped a wide thin mat of foam onto a nonadhesive belt which carried the mat through a stream of warm air flowing across its surface. Since this proved slow, we began extruding spaghetti-like foam elements onto the belt, first in arcs across it, later in lengthwise parallel lines. It was at this point that we designed the first unit for the Winter Haven Laboratory.

Late in 1960, Frank Ginnette, Bob Graham, and I realized that for efficient driers of large capacity, the air must flow through a deep bed of foam. We, therefore, began extruding the foam mat onto perforated plates. By moving the loaded plates over jets, the air pierced the foam mat above each hole. The pseudoplasticity of the foam prevented the foam from falling through the plate perforation originally, or from closing the hole once it had been pierced. The pierced or cratered mats could then be stacked up on an air stream, or better, in two converging air streams, for drying.

In 1961, while our own automatic crater-type drier was still being designed, Norm Sjogren of Chemet Engineers developed a sophisticated pilot plant of his own, using only the concepts described. He then built a large unit, 200 lbs. of product per hour, which is now operating successfully, mainly on tomato. Chemet now offers such units for sale, as well as continuous perforated belt units. At about the same time, a large stack unit was designed and built by Dave Folkin at Gerber Products for eventual use on baby food powders.

In 1963, FMC Corp. began offering a stack type foam-mat drier, based fairly closely on the the Albany design. One small unit was built by FMC for lease. About the same time, AMF adapted an unperforated steel belt drier for foam-mat drying. This design had been originated for drying unfoamed tobacco macerate. They presently offer versions of this unit. Small driers have been built by several other processors in Europe and the United States.

Since 1962, Bob Graham and I have been concerned mainly with product development. We have improved orange, lemon, and lime juice powders and comminuted orange powders

by reducing final moisture to 1 percent by using fine-bodied foams. We have eliminated powder floating and beverage cloudiness by flaking the product between warm rolls bearing an edible lubricant.

We have made full-flavored berry powders by adding sucrose before drying. We have made pumpkin, banana, potato, skim milk, molasses, sodium glutamate, and other powders. We have prepared pineapple and Concord grape powders which await development of a dry essence add-back. We have studied tomato powder extensively. We have now achieved a good storage stability of this labile product in impervious containers. We have traced early disappointments to insufficiently effective exclusion of oxygen from the package. In the case of tomato, such oxygen rapidly fades the powder.

We have suffered a number of failures. Coffee and tea can be nicely foam-mat dried, but only when foamed with sucrose esters, still unacceptable in the United States. Whole milk, without stabilizer, can be dried, only to oxidize in storage. Applesauce powder is too subject to caking.

Foam-mat drying appears to find its best application to a few fruit powders which cannot otherwise be more cheaply dried. Although burning can be avoided by good practice, some stripping of volatiles seems unavoidable--as indeed it is in any form of drying. The suitable products, therefore, do not depend on volatiles for character such as tomato and molasses, or possess a reserve of volatiles, such as citrus peel. In these commodities there will probably be continuously increasing use as raw material preparation, packaging, and marketing become adapted to this process.

DISCUSSION

Question: What basis were you using in designating capacity?

A.I. Morgan: I was referring to dry solids. The largest figure I've heard along those lines in this perforated belt which Mr. Sjogren said can be designed at 1, 200 pounds an hour.

Question: What release agent do you suggest for the compressing rolls?

A.I. Morgan: I think the one we like best for orange is Myverol 18-85--it is the cottonseed oil--Monoglyceride. There are a number of very good release agents--the question is which ones are compatible with citrus.

Question: Does this affect reconstitution?

A.I. Morgan: Yes, it seems to help.

Question: Are there any flavoring extracts that can be added?

A.I. Morgan: Yes, you can obtain very good essence from berries, but its aqueous and we don't know any way of adding an aqueous extract.

The aqueous essences can't be put in the powder, of course, but we and Sunkist only know how to encapsulate oils, but oddly enough in the case of berries the addition of about one-half of the weight of the berry as sucrose before drying seems to capture and retain the flavor in the powder without any further fooling around. We can dry a few things down to where a certain proportion of the powder is crystalline rather than entirely glassy.

Question: With regard to tomato powder, what storage conditions do you find most favorable?

A.I. Morgan: Apparently, one trick is to get the heavy metals out. This seems to result in stabilization with regard to the flavor, odor, and color in storage in a good container. Nothing seems to help if you are going to store it in the presence of oxygen.

RECENT DEVELOPMENTS IN THE USE OF THE FOAM-MAT PROCESS FOR PRODUCTION OF CITRUS POWDERS

by
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Southern Utilization Research and Development Division
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Winter Haven, Fla.

(Presented by R. E. Berry)

Research concerning use of the foam-mat process for producing citrus powders has centered around four principal areas. The first of these is a study of the storage stability of orange and grapefruit powders made under different production conditions. This has included the study of different storage conditions as well. Secondly, research has centered around a study of certain characteristics of concentrates, and the relative effect of these on drying behavior, and nature of the powder produced from them. A study of the factors affecting rate and ease of reconstitution has comprised the third area. Finally, a study of powders, compared to the parent concentrates, has been carried out on a more fundamental basis involving the use of chromatographic procedures.

In the determination of storage stability of orange and grapefruit powders, the use of antitoxidants did not appear to enhance storage stability. To check the influence of oxygen more thoroughly, further investigations are presently under way using oxygen scavengers. In other storage studies, grapefruit powders have been stored up to 12 weeks without developing detectable flavor changes at 85°F., and have been stored for over 35 weeks at 70°F. without flavor changes. These flavor tests are based upon minimum discrimination of differences, and acceptability of the powders would go well beyond these storage times. Extensive storage tests have been started on both grapefruit and orange powders covering a wide range of temperatures, packaging materials, and packaging atmospheres.

Drying characteristics of concentrates were found very closely related to foam bubble size and structure. In studies of foaming agents and sizes of bubbles, several different type agents have been used successfully for the production of foams with good drying characteristics. A method of determining approximate average bubble size has been developed for use in evaluation of the suitability of foams for drying.

The powders produced from different type foaming agents have been compared for flavor, moisture content, drying characteristics, reconstitution, and general appearance. Myverol 18-00 was found to be most beneficial for moisture release, probably due to formation of very fine bubble structure. From the standpoint of reconstitution ease and appearance, however, soya albumin (D-100) and Methocel-10 were found most effective.

Experimental drying runs have been carried out using several different additives to determine the effect on flavor and physical character of powders. These included the addition of orange "essence" to foam, before drying, and the use of orange concentrate to which peel oil had been added prior to canning. The addition of nootkatone to grapefruit concentrate before drying was also tried to determine the effect on flavor of the powder. Orange essence was found to be more effective toward improvement of flavor when added directly to the dried powder as a nonaqueous extract than when added to the foaming ingredients. The use use of orange concentrate, to which peel oil had been added, was found to result in less efficient moisture removal during drying. This served to substantiate previous findings. The addition of nootkatone, isolated from grapefruit peel oil, to grapefruit concentrate prior to

foaming resulted in a considerable improvement in flavor of the grapefruit powder.

Studies on reconstitution have involved development of a densitizing treatment to increase bulk density of the powder. Temperature, release agents, and conditions for densitizing both orange and grapefruit powders have been developed by using a double-drum dryer adapted for the purpose.

Packaging studies using vacuum equilibration and carbon dioxide atmosphere have also been found to improve reconstitution and to impart a better appearance to the reconstituted juice.

Analytical studies have been carried out on orange powders. The parent concentrate has been compared to orange powders stored at 0°F. possessing good flavor, and to powders that had been stored at 100°F. until strong "off-flavors" and "off-odors" developed. These studies have utilized gas, thin-layer and column chromatography techniques. They have included preliminary investigations of sugar and glycoside, acid, phenolic, and carotenoid fractions. There appears to be some relation between "off-odors" and carotenoid fractions. The acidic fraction has shown some indications of differences between the "off" powders and control powders. None of the fractions studied have indicated any differences between the parent concentrate and control powders.

In other recent developments, concentrates have been made from late season Valencia oranges. These experimental concentrates have been prepared with gross viscosities which varied over a wide range. They differ greatly in pulp content as well. These concentrates are to be used for preparation of powders using the "crater" dryer.

The new "crater" dryer has been received, installed, and is in operation. It is capable of producing good quality powders at a rate of approximately 25 pounds per hour. A few preliminary powders have been prepared but optimum conditions have not been fully developed yet.

DISCUSSION

Question: Do you notice any change in color after storage of these powders?

R.E. Berry: We haven't noticed very much--there is very slight darkening in orange, but only in very extensive storage.

Question: Have you studied the relationship between oil content and bubble size?

R.E. Berry: We have not studied this specifically, but of course I would expect so. There is a correlation in that the smaller the bubble size the dryer it gets, and the larger the bubble size the higher the moisture content of the powder--also the more oil you put in it the less completely it dries. Yes, there is a relationship between oil and bubble size.

Question: How do you determine solution time?

R.E. Berry: We have one man stand by with a stopwatch and another man mixes. He pours the powder in a beaker and then pours the water in. He starts the stopwatch as soon as stirring starts and as soon as, in their judement, there are no remaining undissolved particles the stopwatch is turned off.

Question: At what temperature do you check solubility?

R.E. Berry: Forty degrees Fahrenheit. We have checked the solubility of these powders in other temperatures and we find the higher the temperature of the water, as you would expect, the more quickly it goes into the solution. At room temperature the powder dissolves more rapidly.

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